

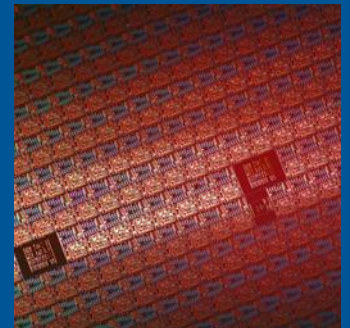


Accelerating the next technology revolution

Systematic Study of New Chemistries For EUV Mask Cleaning

Ruhai Tian, Abbas Rastegar,
Matthew House

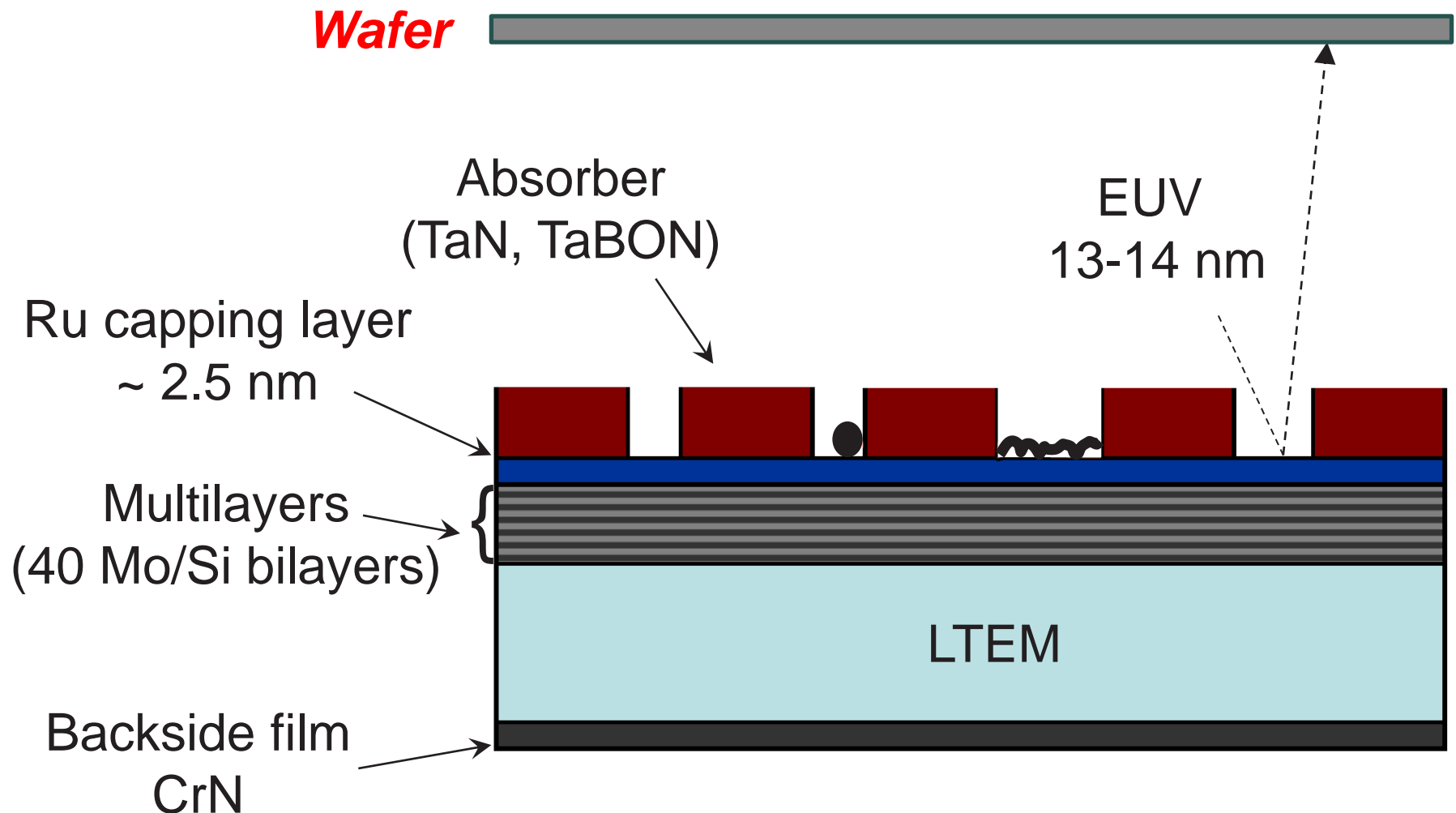
10/01/2012



Outline

- ❑ EUV mask structure and contamination
- ❑ Introduction of conventional cleaning chemistry
- ❑ Issues of EUV mask cleaning with conventional chemistry
- ❑ Screening of chemicals used for surface cleaning
- ❑ Evaluation of EKC 830 for Ru/ML cleaning
- ❑ Conclusions
- ❑ Future work

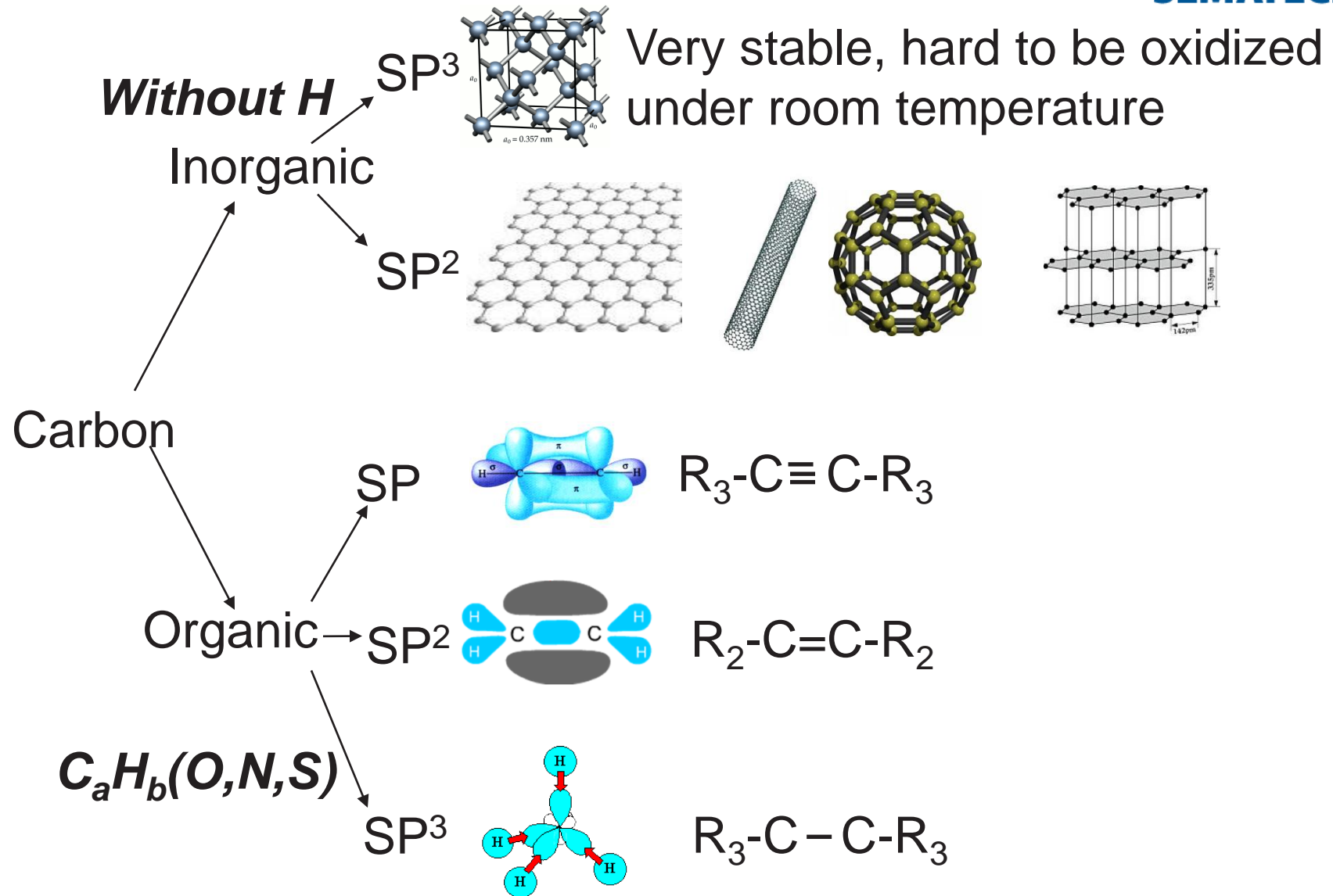
EUV mask structure and working principle



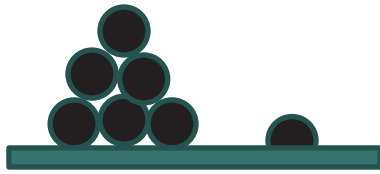
Contamination of EUV masks

1. Can be contaminated in air, N_2 , and vacuum and during storage, handling, and production
2. Can be contaminated by organic and inorganic materials (metal, oxide, etc.)
3. Carbon is one of the main components; it has many allotropes
4. Every 1 nm C deposition results in a 1% EUV reflectivity drop; nanoparticles can be printed on the wafer

Carbon chemistry



Mechanism for carbon removal



Physical stacking
Embedding



Chemical bond

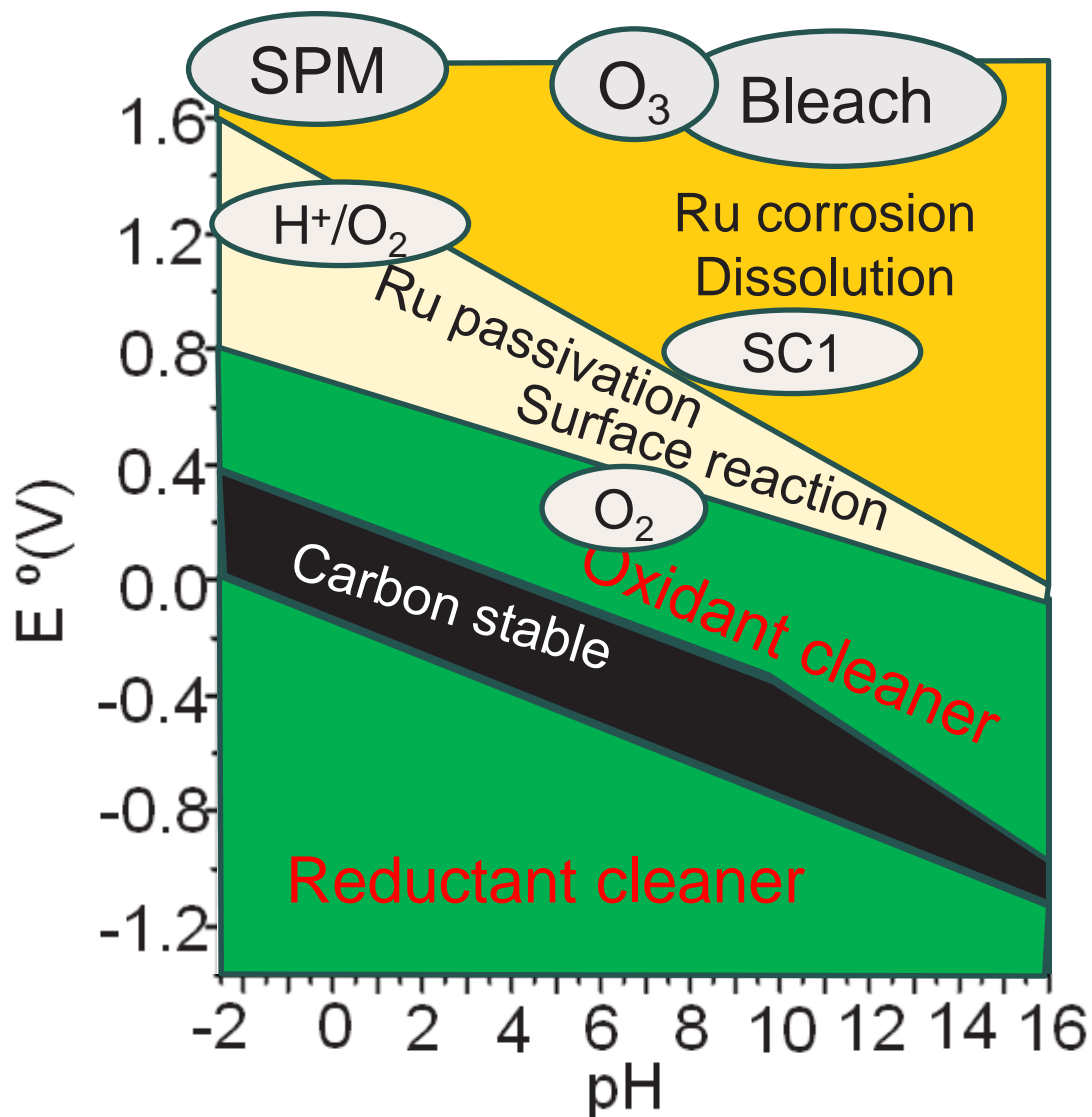


Electrostatic interaction

Approaches to remove carbon

- ☐ Can be oxidized to get volatile molecule pieces
- ☐ Can be oxidized to get soluble molecules $R_2-C=O$, $R-COOH$, CO_2
- ☐ Some chemical bonds can be hydrolyzed under an acid or base condition (e.g., ester groups)
- ☐ Surface charge of the carbon surface can be tuned by acid/base or surfactant
- ☐ They show different solubility in different solvents

Pourbaix diagram of Ru vs. C (graphite)



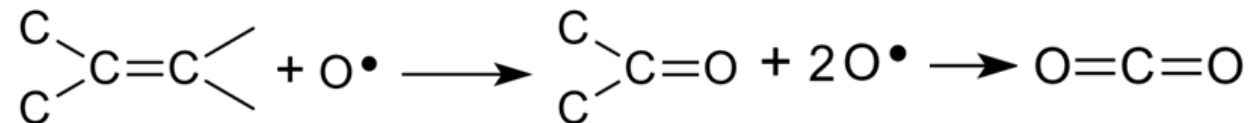
1. The Ru layer is more stable when an oxidant is used under acidic conditions
2. Ru has a larger stability window than graphite

Conventional cleaning chemistry (RCA)

Chemical formulation	Composition	Temperature	Cleaning Purpose
Piranha (SPM)	$\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2=2:1$ to $4:1$	80-130 °C	Organic
SC1 (APM)	$\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:5$ to $1:2:7$	75-85 °C	Organic & metal
SC2 (HPM)	$\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:6$ to $1:2:8$	75-85 °C	Oxide
Ozonated DI water	6-120 ppm	Room	Organic
BHF (BOE)	NH_4F (40 wt%): HF (49 wt%)=7:1	Room	Oxide (SiO_2)

Cleaning mechanism

SPM and DI- O_3 : generation of oxygen radicals and oxidation reaction



SC1: oxidation, reaction, etching, and metal- NH_3 complex formation

SC2: reaction of base/oxide with acid

BOE: reaction and etching

Compatibility of conventional chemistries for EUV mask cleaning



Chemical	Purpose	Disadvantages
SPM (Piranha)	Particle removal Organic removal	Particle adders
		Etch TaN and CrN materials
		Hard to remove inorganic carbon
		Surface contamination by S
Ozone	Organic removal	Surface oxidation
SC1	Particle removal Organic removal	Poor performance for stable organics
SC2	N/A	Etch metal
BHF (BOE)	Oxide removal	Etch TaN, CrN

New chemistries for EUV masks

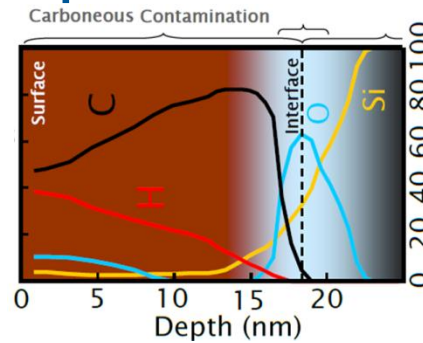
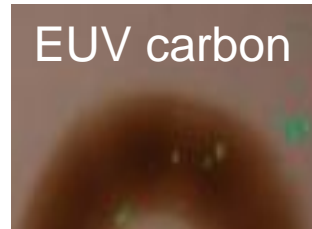
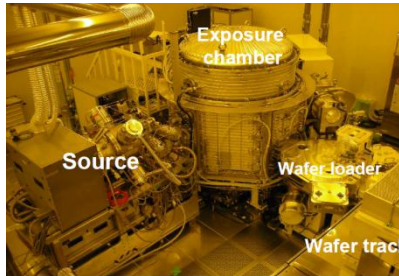


- ☐ Remove particles Remove organics
- ☐ No reflectivity loss (contamination; surface oxidation); no CD loss; no particle deposition
- ☐ Easy to use; compatible with tool materials

Oxidants	Strong acids	Strong bases	Polar Solvents	Surfactant
O ₃ (H ⁺)	HCl (12 M)	EKC 830	IPA	0.1M SOD
H ₂ O ₂ (H ⁺)	NCW1002	KOH	Acetone	0.01M SOD
0.1M KMnO ₄	HF	28-30% NH ₄ OH	DMSO	
O ₂ (H ⁺)		0.1M KOH	DMF	
I ₂		5% NH ₄ OH	NMP	
O ₂ (H ₂ O)		PG remover	DI	
96% H ₂ SO ₄		Bleach		
SPM		EKC 265		
Aqua fortis				

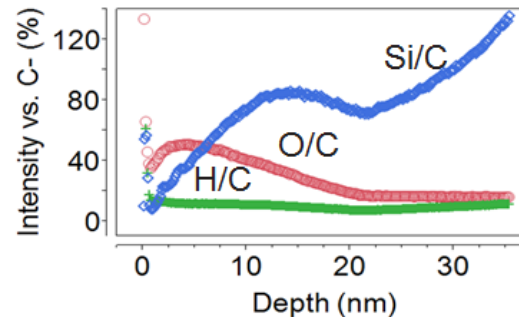
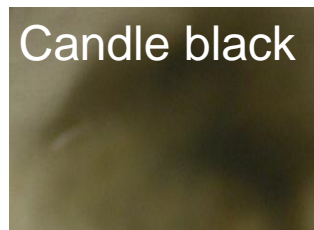
Numerous chemical screenings!

A simple way to simulate EUV carbon deposition—candle black deposition



XPS results by Iwao Nishiyama et al., Feb, 26, **2007** IUEVI Optics Contamination, San Jose

□ The same element composition, i.e., H, O, Si



□ Similar depth profiles

TOF SIMS results by Sematech



VS.



Days vs. Minutes

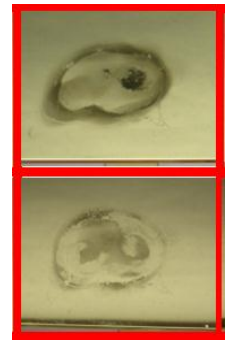
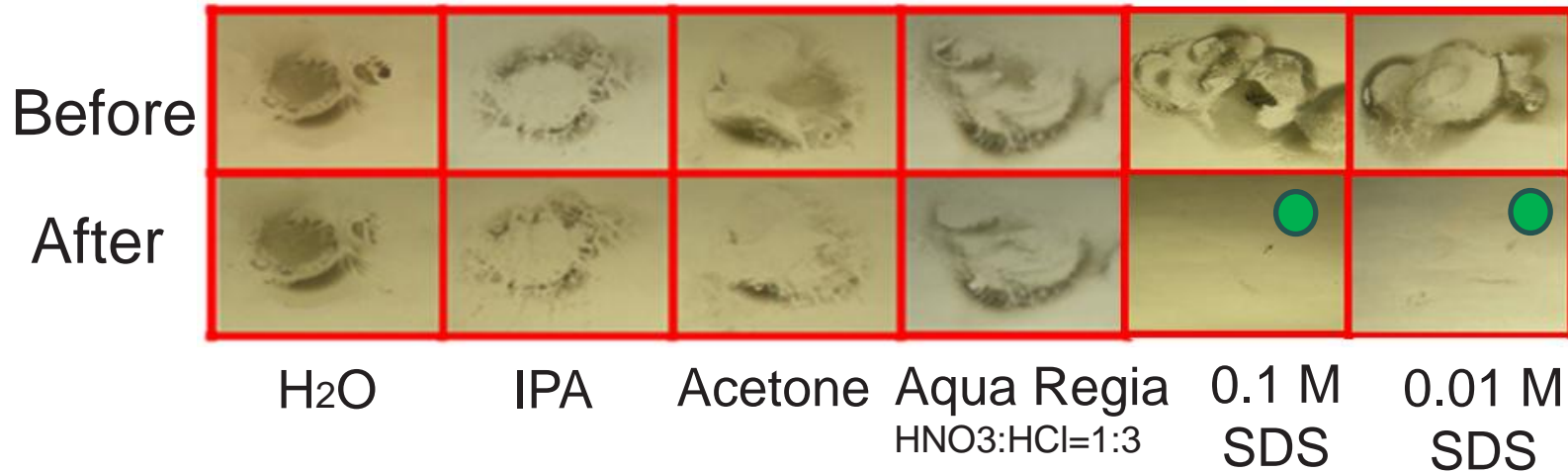
Chemical screening chart



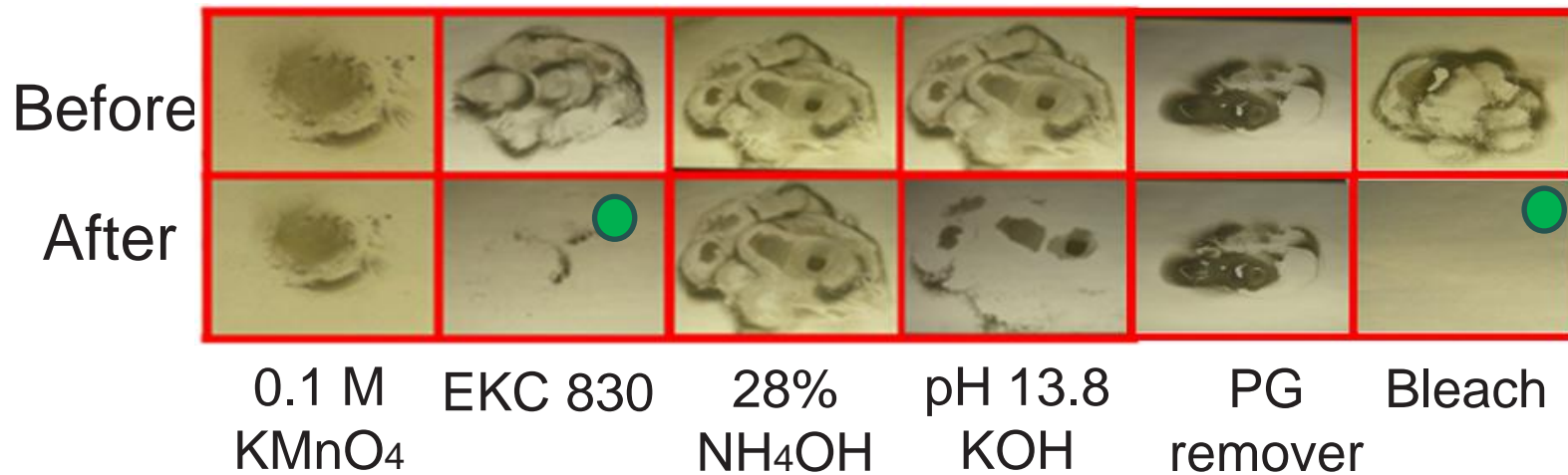
	Chemical	E ⁰	pH	20 °C 30 mins	50 °C* 30 mins	100 °C* 30 mins	Boiling 30 mins	Reflectivity loss** (%)	Substrate etch (Macro scale)
Oxidants Strong acids	O ₃ (H ⁺)	2.08V	-	-	-	-	-	>3%	Surface oxidation
	H ₂ O ₂ (H ⁺)	1.78V	-	-	-	-	-	-	No etch
	0.1M KMnO ₄	1.51V (H ⁺)	8.75	N	N	N	N	1.01	Etch ML and CrN
	O ₂ (H ⁺)	1.23V	-	-	-	-	-	-	No etch
	I ₂	0.54V	-	N	-	-	-	-	No etch
	O ₂ (H ₂ O)	0.4V	-	N	N	N	N	-	No etch
	96% H ₂ SO ₄	0.16V	-	N	-	-	-	-	No etch
	SPM	-	-2.00	-	-	Y+++	-	-	No etch
	Aqua fortis	-	-1.09	N	-	N	-	1.01	No etch
	HCl (12 M)	-	-1.10	N	-	-	-	-	No etch
	NCW1002	-	3.28	-	-	Y+	-	-	No etch
	HF								Etch ML and CrN
Strong bases	EKC 830	-	14.37	Y++++	-	Y++++	-	0.94	No etch
	KOH		13.80	Y+++					No etch
	28-30% NH ₄ OH		13.77	N	-	-	-		No etch
	0.1M KOH	-	12.75	-	-	Y++++	-	-	No etch
	5% NH ₄ OH	-	12.00	-	-	-	Y++++	-	No etch
	PG remover	-	11.82	Y+	Y++	-	-	-	No etch
	Bleach		11.73	Y++++			-	>3%	Etch ML
	EKC 265	-	11.70	-	-	Y+++	-	0.32	No etch
Polar Organic solvents and DI	SC1			N			-	-	No etch
	IPA	-	-	N	-	-	-	-	No etch
	Acetone	-	-	Y+	-	-	-	1.01	No etch
	DMSO	-	-	N	Y++	Y+++	-	-	No etch
	DMF	-	-	-	Y+++	-	-	-	No etch
	NMP	-	-	-	-	Y++	-	-	No etch
Surfactant	DI			N	N	N	N	0	No etch
	0.1M SOD		6.49	Y++++	-	-	-	0.14	No etch
	0.01M SOD		6.49	Y++++	-	-	-	-	No etch

* The temperature is measured on hotplate a surface ** EUV reflectivity loss after immersion for one hour

Candle black cleaning with different chemicals at room temperature for 30 minutes

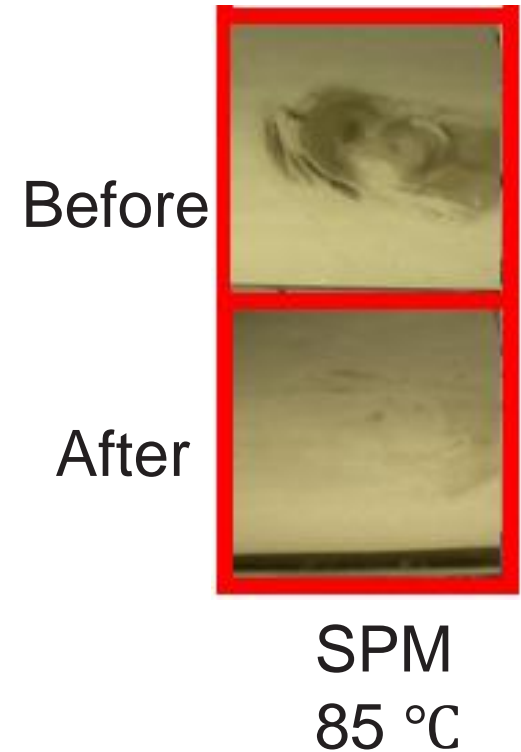
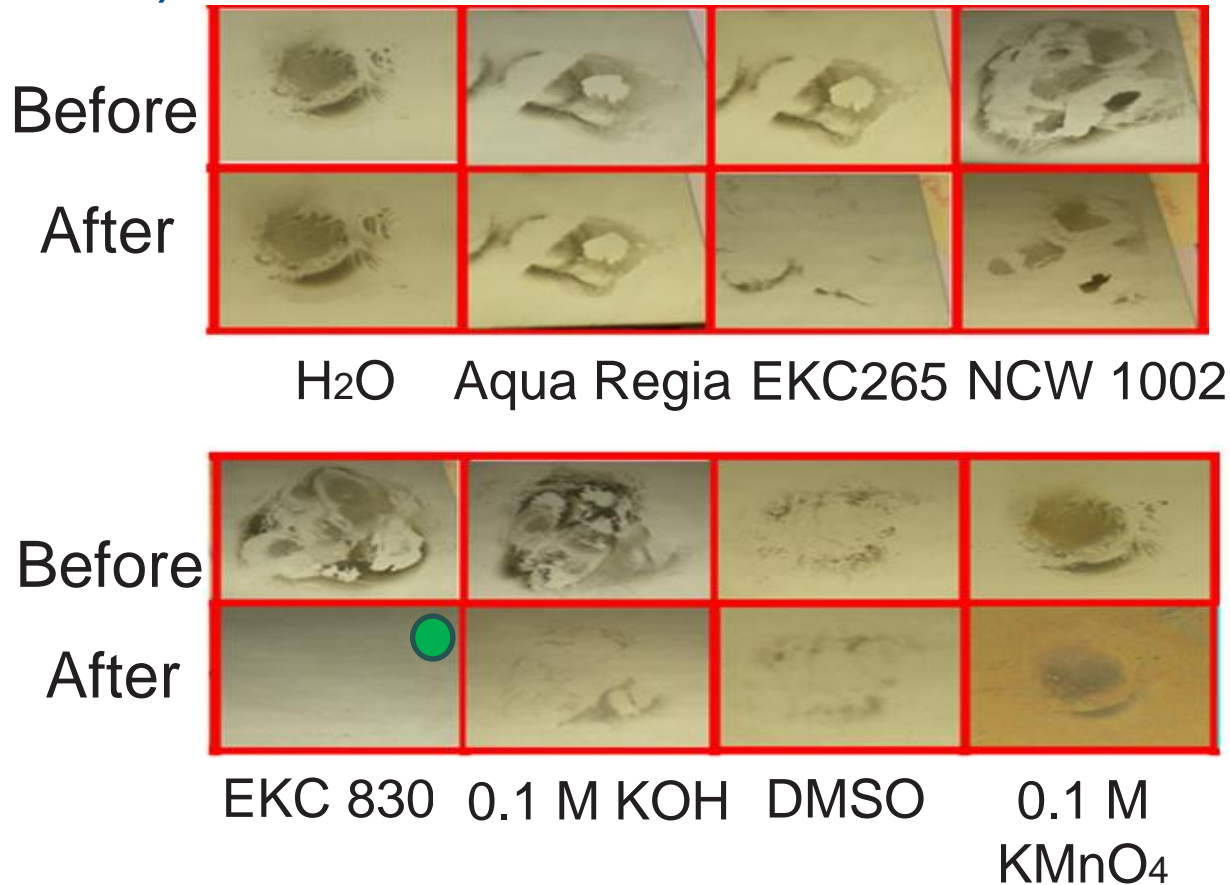


SC1



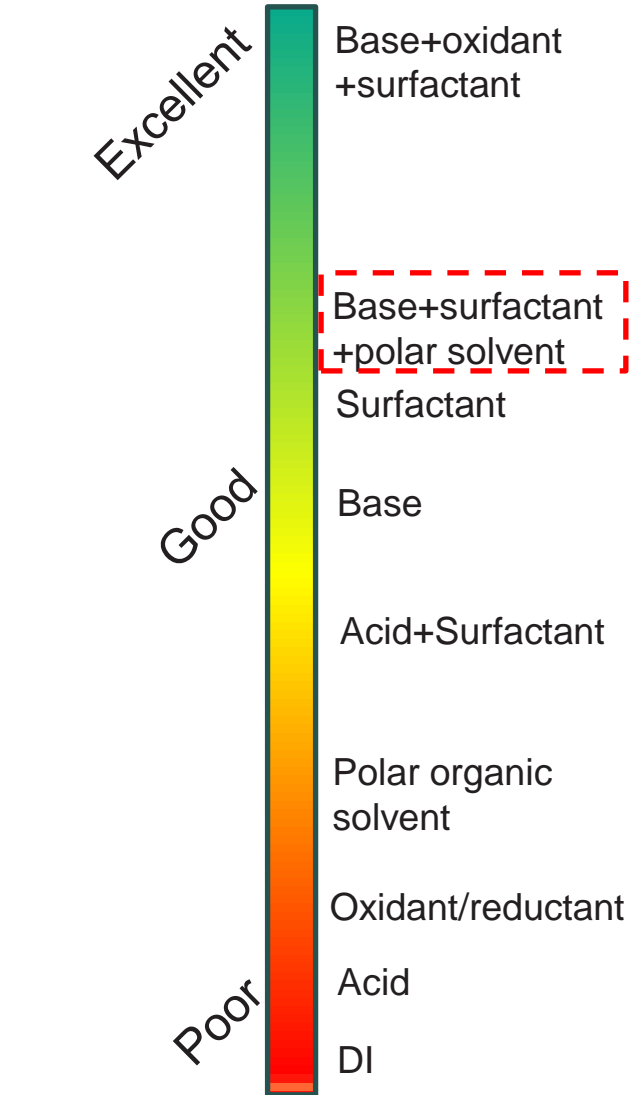
SDS: Sodium dodecyl sulfate; PG remover and EKC 830 are commercially available

Candle black cleaning with different chemicals at higher temperature for 30 minutes (plate 100 °C)

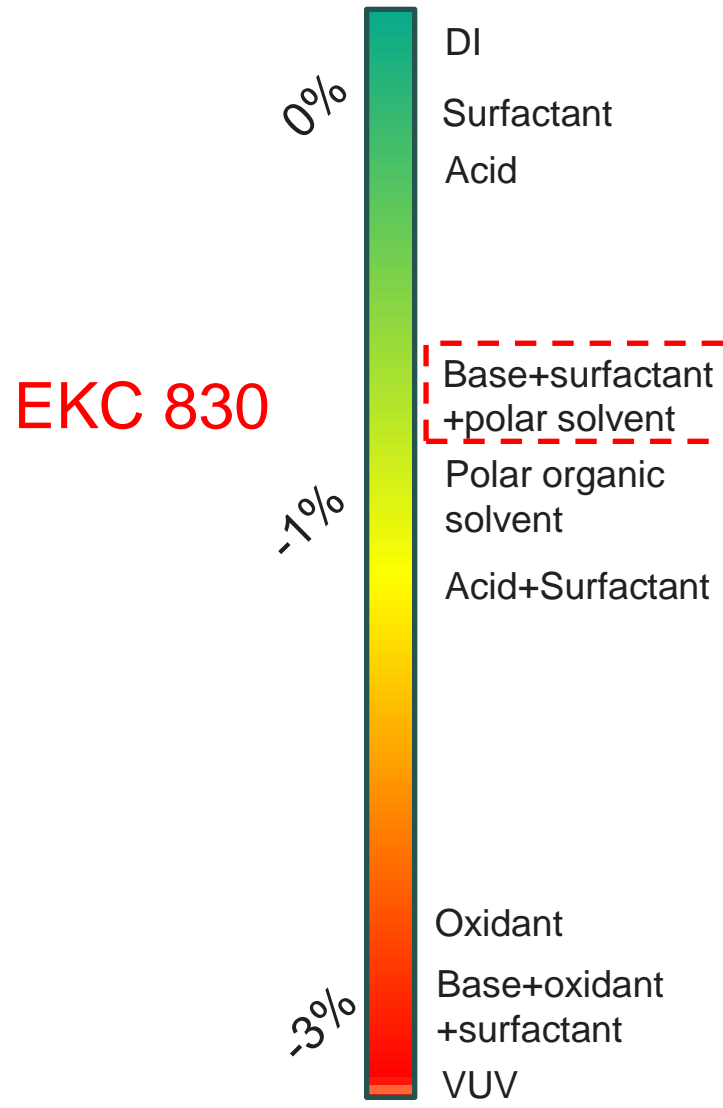


EKC 265, NCW 1002, PG remover, and EKC 830 are commercially available

Chemicals vs. cleaning effect & reflectivity



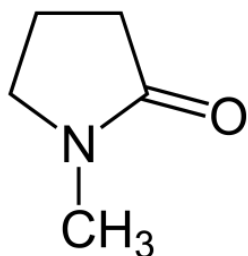
Carbon removal efficiency



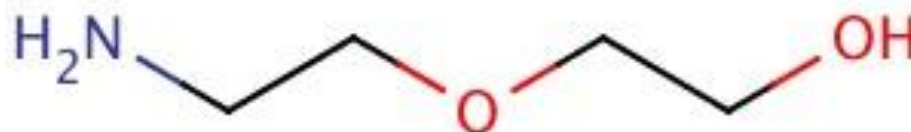
EKC 830

Chemical-induced EUV reflectivity loss

Formulation of EKC 830 and effect on blank reflectivity



n-Methylpyrrolidone (NMP)



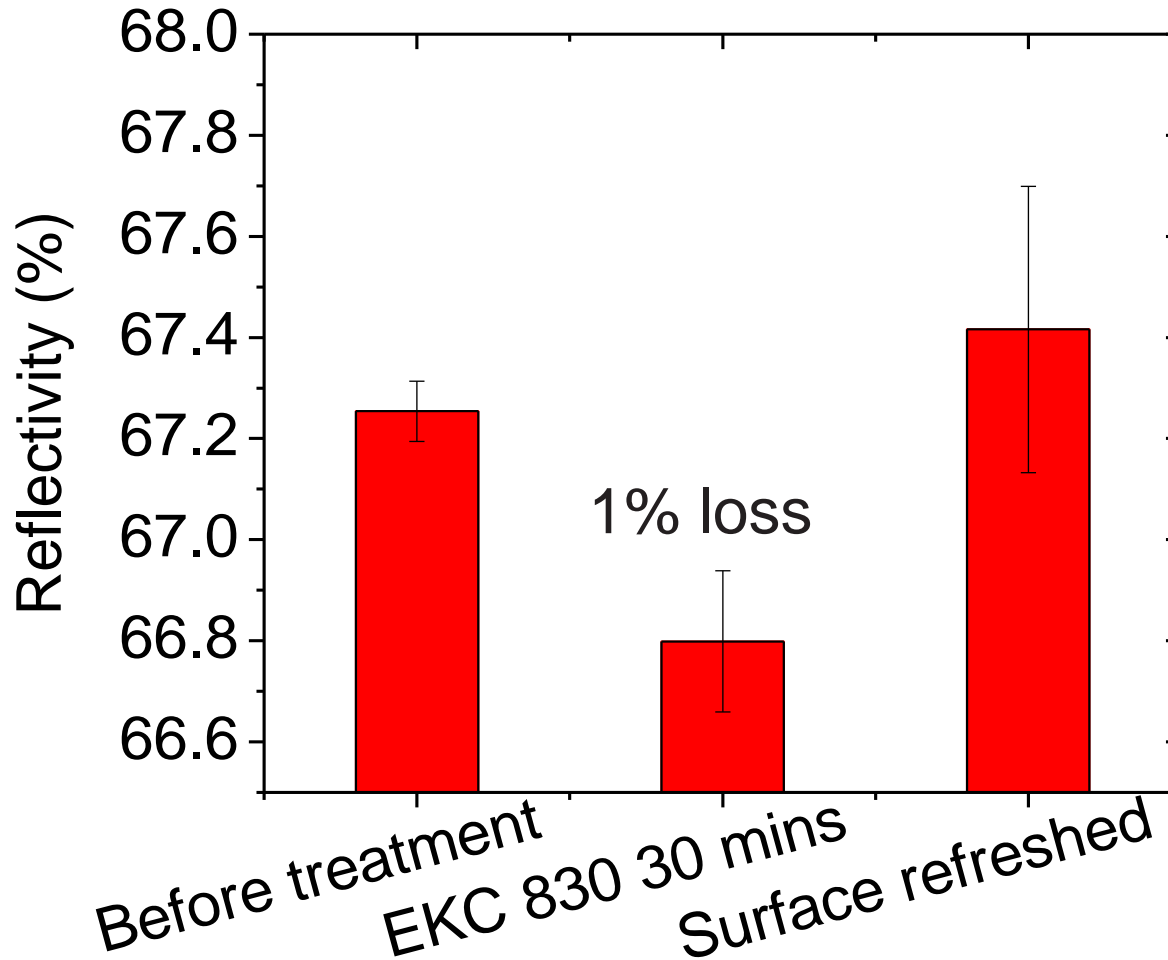
2-(2-Aminoethoxy)ethanol

...

Unknown parts

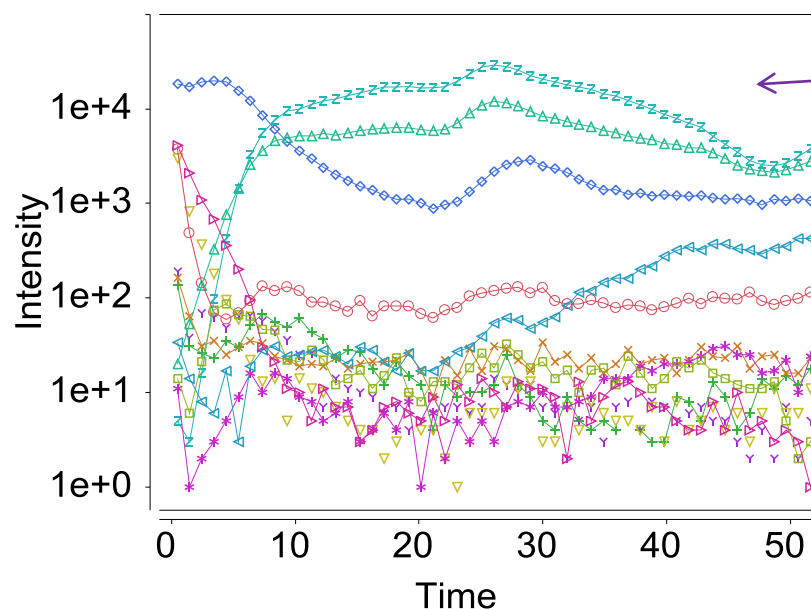
- ❑ Strong base: pH 14.3
- ❑ Polar solvent: NMP
- ❑ Surfactants: ?

Compatibility of mask material with EKC 830

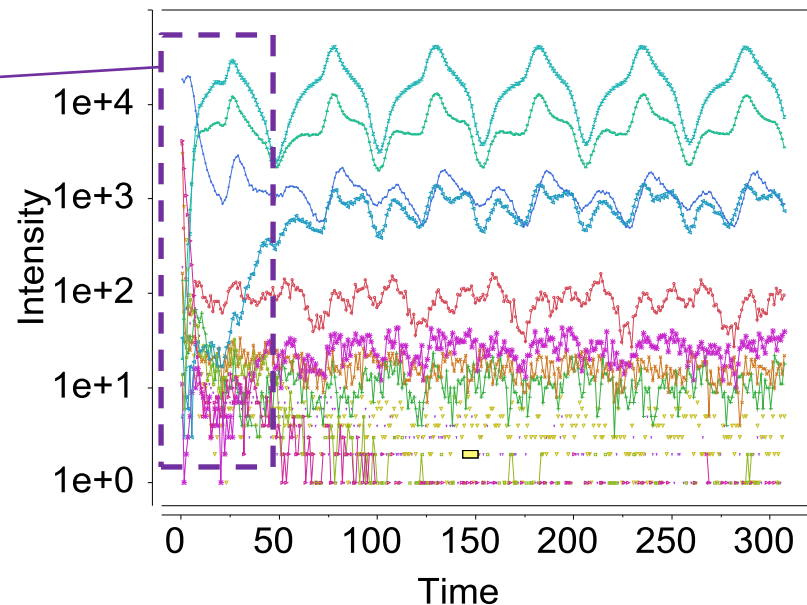


EKC 830 treatment degrades EUV reflectivity but it is recoverable

Material compatibility with EKC 830



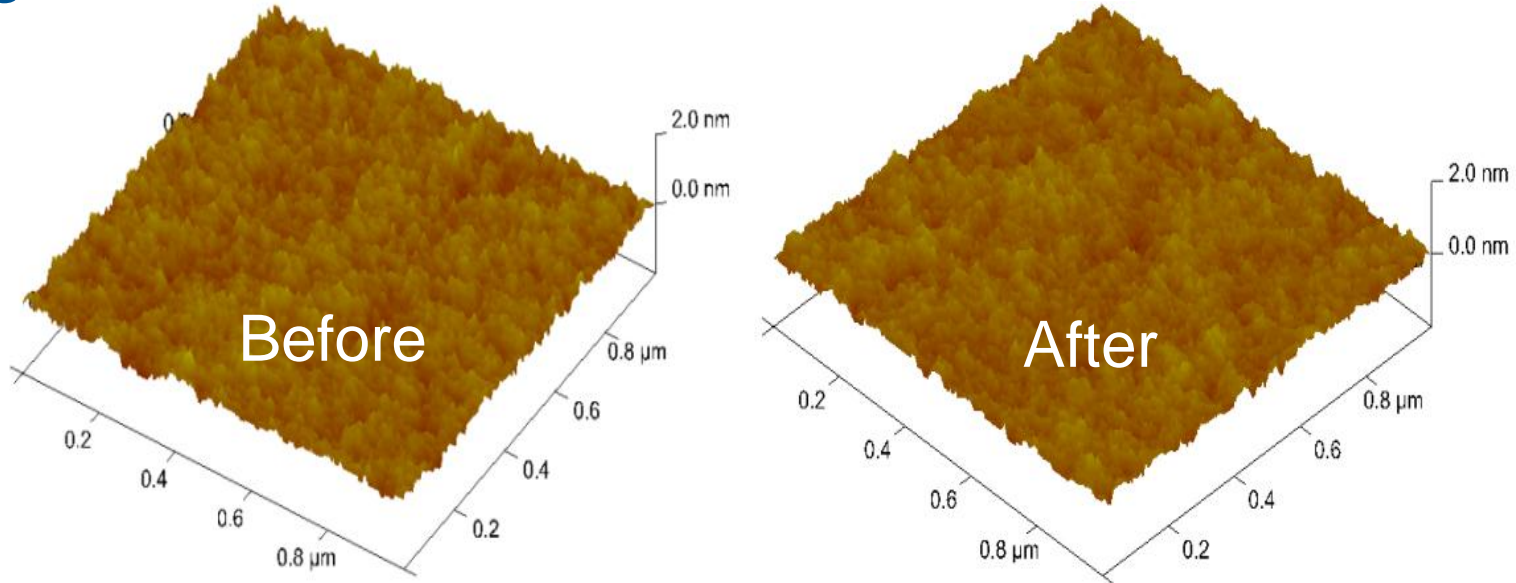
Intensity ○ H- + C- ◇ O- × F- △ Si- ▼ S- ▽ Cl- z Si_2-
* Mo- □ Ru- ◀ MoSi- ▶ RuO_2-



Intensity ○ H- + C- ◇ O- × F- △ Si- ▼ S- ▽ Cl- z Si_2-
* Mo- □ Ru- ◀ MoSi- ▶ RuO_2-

- ❑ EKC830 does not etch the multilayer structure
- ❑ No etching of absorber material (TaN) was observed when 100 nm nanopattern features are used for testing

Influence of EKC 830 treatment on surface roughness



Chemical	Rq (nm)	Ra (nm)	Rmax (nm)
Reference	0.126	0.093	1.160
EKC 830	0.112	0.080	0.963

No effect on Ru-capped ML roughness

Conclusions

1. Different types of chemicals/formulations have been screened.
2. Among all chemistries, according to the screening results, a formulation of base, surfactant, and polar solvent is able to remove carbon contamination with little influence on EUV reflectivity.
3. The best carbon removal was observed with chlorine chemistry under a base condition. However the ML structure can be damaged.
4. Further tests will be tried with reduction chemistry.

Acknowledgements



SEMATECH technical support:

Lenny Gwenden

Nancy Lethbridge

Edward Maillet

Patrick Kearney

Andy Ma

Teki Ranganath

Alin Antohe

Vibhu Jindal

Chemical formulations from EKC technology

Questions?

